Potential for the use of hydroxylamine derivatives as wood preservatives

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Abstract

The potential of 17 hydroxylamine derivatives as wood preservatives was assessed on ponderosa pine sapwood blocks exposed to one of two decay fungi: *Gloeophyllum trabeum* or *Trametes versicolor*. Weight losses on untreated controls were generally lower with the white-rot fungus (*T. versicolor*) averaging 30.4 percent, while those for the brown-rot fungus (*G. trabeum*) were 72.0 percent. None of the test chemicals completely inhibited weight loss, although one chemical was associated with lower weight losses at the highest concentration tested. The results suggest that the hydroxlamine derivatives evaluated have little potential as wood preservatives.

Conventional wood preservatives have provided excellent protection against wood-degrading organisms; however, increasing public mistrust of these chemicals has encouraged a search for alternative wood protection strategies that take advantage of the physiological capabilities of the target organisms. One approach is to use chelators to sequester elements required by fungi to initiate the decay process. Oxalic acid is produced by nearly all brown-rot fungi and its presence is believed to be necessary for the initiation of decay. Competitive compounds can negate the role of oxalic acid, thereby limiting decay initiation (Viikari and Ritschkoff 1992). Green et al. (1997) reported that the chelator N,N-naphthaloylhydroxylamine sharply reduced both fungal decay and termite attack of southern pine (*Pinus* spp.) sapwood. This report describes laboratory trials of 17 other hydroxylamine derivatives against white- and brown-rot fungi.

Materials and methods

The efficacy of the compounds was examined by using a scaled-down version of the soil block test (AWPA 1999) developed by Scheffer et al. (1987). Ponderosa pine sapwood (*Pinus ponderosa* Laws.) samples (10 by 10 by 5 mm long) were ovendried (104°C) and weighed (nearest 0.001 g), then treated with solutions of 0.5, 1.0, or 2.0 percent of 1 of 17 compounds (**Table 1**) using a double vacuum process (20 min. @ 800 kPa vacuum, drop solution, release vacuum, apply 20 min. vacuum, and release). The blocks were then blotted dry and reweighed to determine net solution uptake, then covered with moist paper and left for 24 hours at room temperature (21° to 23°C) to allow any wood/ chemical reactions to proceed. The blocks were ovendried (104°C) and weighed. Each treatment was replicated on 12 blocks.

The blocks were then placed into sealable plastic bags and sterilized by exposure to 2.5 mrads of ionizing radiation from a cobalt 60 source.

Decay chambers were 30-mL glass bottles, which were half filled with a moist garden loam. A 10- by 10- by 2-mm-long thick strip of red alder (*Alnus rubra* Bong.) for the white-rot fungus or western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) for the brown-rot fungus was placed on the surface, then the jars were loosely capped and autoclaved for 45 minutes at 121°C. After cooling overnight, the jars were autoclaved for 15 minutes at 121°C to kill any spore-forming bacteria.

The decay chambers were inoculated with agar discs cut from cultures of either the white-rot fungus *Trametes versicolor* (L. ex. Fr.) Pilat (Isolate Madison R105) or the brown-rot fungus *Gloeophyllum trabeum* (Pers. ex. Fr.) Murr. (Isolate Madison 617). The bottles were then capped and incubated un-

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Table 1. — Chemicals evaluated as potential wood preservatives in a soil block test.

Chemical	Abbreviation	Source
4-chloro-N-hydroxyacetanilide	4-CNHA	Li et al. (200_)
2-chloro-N-hydroxyacetanilide	2-CNHA	
2-chloro-6-methyl-N-hydroxyacetanilide	CMNHA	
N-hydroxyacetanilide	NHA	
N-hydroxybutyroylacetanilide	NHB	
N-hydroxy-tert-butyroylacetanilide	NHTB	
N-nitroso-N-phenylhydroxylamine	NNPH	Sigma Chemical
N,N-dimethylformamide (used as a co-solvent)	DMF	
1-hydroxybenzotriazole	1-HBT	Aldrich
3-hydroxy-1,2,3-benzotriazin-4-(3H)-one	HBTO	
1-hydroxyl-7-azabenzotriazole	HABT	
N-hydroxyl-5-norbornene-2,3 dicarboxylic acidimide	HNDAI	
2-hydroxypyridine-1-oxide	HPO	
N-hydroxyphthalimide	NHPI	
ciclopirox olamine	CPOA	
N-Benzoyl-N-phenylhydroxylamine	BPHA	
1-hydroxypyrazole	HP	Begtrup and Vedso (1995)
4-hydroxy-2H-1,4-benzoxazin-3-one	HBA	Atkinson et al. (1991)

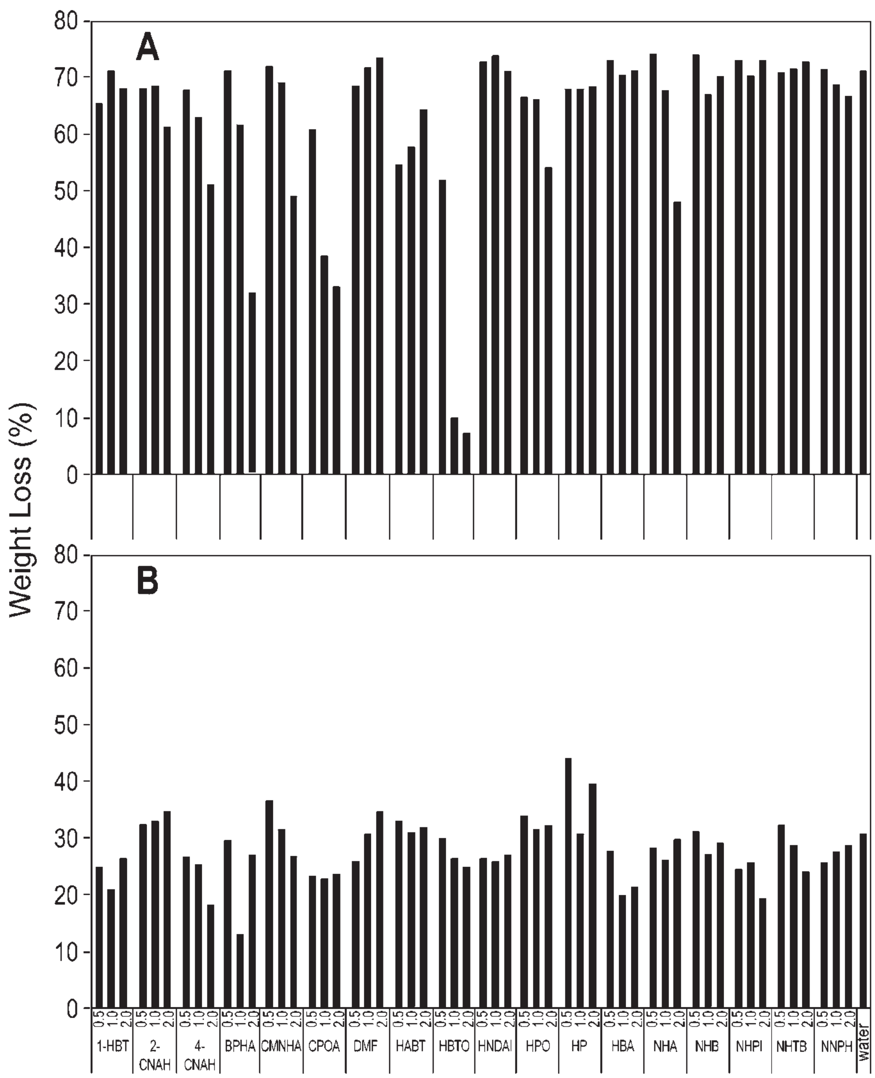

Figure 1. — Weight losses of southern pine blocks treated with selected chemicals and exposed to G. trabeum (A) or T. versicolor (B) in a soil block test.

til the fungus had thoroughly colonized the strip. Test blocks (one/ bottle) were then placed (cross section downward) on the feeder strips and the bottles were incubated at 28°C and 90 percent relative humidity. Untreated control blocks were periodically removed to monitor the course of decay and all chambers were harvested when control weight losses had exceeded 60 percent for the brown-rot fungus or 30 percent for the white-rot fungus. Six blocks were evaluated for each fungus/ chemical concentration combination.

At the end of the exposure, the test blocks were removed from the chambers, scraped clean of adhering mycelium or soil, and weighed. The blocks were then ovendried (104°C) prior to being weighed. Weight loss over the exposure period served as the measure of chemical effectiveness.

Results and discussion

Weight losses of untreated control blocks exposed to *G. trabeum* and *T. versicolor* averaged nearly 72 and 30.4 percent, respectively, indicating that conditions were ideal for fungal attack (**Fig. 1**). Lower weight losses in blocks exposed to *T. versicolor* probably reflect the use of pine test blocks.

Weight losses in blocks treated with the test chemicals and exposed to *G. trabeum* often exceeded 50 percent, suggesting that most of the hydroxylamine derivatives had little protective effect. The exception was 2 percent HBTO; blocks treated with this chemical experienced only 7.5 percent weight loss when exposed to *G. trabeum*. The results with HBTO also implied a dose response. Slight dose effects were also noted with BPHA and CPOA, but the weight losses at the highest treatment concentrations of the latter two chemicals were still well above those considered to represent protection from fungal attack.

Weight losses in treated blocks exposed to *T. versicolor* were far lower than those found with *G. trabeum*, reflecting the tendency for white-rot fungi to cause higher weight losses on hardwoods. In addition, there was little evidence of a dose effect with any of the chemicals tested. These results suggest that the hydroxylamine derivatives used in our study lacked the protective effects found by Green et al. (1997) with N,N-naphthaloylhydroxylamine.

Hydroxamic acids are known to be highly active against fungi, bacteria, and some pests (White and Hill 1943, Neilands 1967, Weisburger and Weisburger 1973, Chatterjee 1978, Rather and Hänel 1990, Thackary et al. 1990, Xie et al. 1990, Givovich and Niemeyer 1991) but the specific modes remain poorly understood. Green et al. (1997) suggested that precipitation of a complex between NHPI and calcium on the torus of pit membranes prevented attack of pectins in the pit membrane by fungal endopolygalacturonases, thus limiting the ability of the fungus to move from cell to cell. Our results suggest that the metal-chelating capacity of hydroxamic acids cannot explain different fungal decay rates.

The inability of the various derivatives to provide some level of protection was perplexing. Green et al. (1997) used blocks that were 19 mm long in the grain direction, while our blocks were far shorter and created a much more severe leaching exposure. Most of the chemicals tested exhibited some level of water solubility, making them more likely to leach during the soil block exposure. This suggests that these chemicals would perform poorly as wood preservatives in leaching exposures. The use of copper to sequester the derivative might reduce leaching, but would defeat the goal of moving to metal-free preservatives.

Conclusions

The hydroxylamine derivatives evaluated were apparently incapable of providing consistent protection to ponderosa pine blocks against white-rot or brown-rot fungi under the conditions employed.

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